



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :

C09K 19/54, C08F 220/00, C09K 19/38

A1

(11) International Publication Number:

WO 96/25470

(43) International Publication Date:

22 August 1996 (22.08.96)

(21) International Application Number:

PCT/EP96/00646

(22) International Filing Date:

15 February 1996 (15.02.96)

(30) Priority Data:

95102197.1

17 February 1995 (17.02.95)

EP

(34) Countries for which the regional or
international application was filed:

GB et al.

(71) Applicant (for all designated States except US): MERCK
PATENT GMBH [DE/DE]; Frankfurter Strasse 250, D-
64293 Darmstadt (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): COATES, David
[GB/GB]; 87 Sopwith Crescent, Merley, Wimborne, Dorset
BH21 3SW (GB). GREENFIELD, Simon [GB/GB]; 2
Blackbird Close, Creekmoor, Poole, Dorset BH17 7YA
(GB). JOLLIFFE, Emma, Jane [GB/GB]; 48 The Wood-
peckers, Broadwey, Weymouth, Dorset DT3 5RS (GB).(81) Designated States: JP, KR, US, European patent (AT, BE, CH,
DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

*With international search report.**Before the expiration of the time limit for amending the
claims and to be republished in the event of the receipt of
amendments.*

(54) Title: POLYMERIC FILM

(57) Abstract

The invention relates to a polymeric film composed of an optically anisotropic material made from a cross-linked synthetic resin composition comprising a polymer network, being obtainable by copolymerization of a mixture comprising (a) at least one monomer or oligomer, each of said monomers or oligomers having at least two polymerizable functional groups selected from the group consisting of (meth-)acrylate ester, epoxy and vinyl ether, (b) at least one achiral liquid crystalline monomer or oligomer, each of said monomers/oligomers having mesogenic groups and one polymerizable functional group selected from the group consisting of (meth-)acrylate ester, epoxy and vinyl ether.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Polymeric Film

5 The invention relates to a polymeric film composed of an optically anisotropic material made from a cross-linked synthetic resin composition comprising a polymer network, being obtainable by copolymerization of a mixture comprising

- 10 (a) at least one monomer or oligomer, each of said monomers or oligomers having at least two polymerizable functional groups selected from the group consisting of (meth-)acrylate ester, epoxy and vinyl ether,
- 15 (b) at least one achiral liquid crystalline monomer or oligomer, each of said monomers/oligomers having mesogenic groups and one polymerizable functional group selected from the group consisting of (meth-)acrylate ester, epoxy and vinyl ether,
- (c) a photoinitiator,
- 20 (d) additives selected from inhibitors and accelerators,
- (e) optionally at least one chiral component, and
- 25 (f) optionally at least one liquid-crystalline mono- or dithiol compound, and
to a display device comprising such a polymeric film.

A similar display device is described in European Patent 0 246 842.

30 Chirality in liquid-crystalline materials leads to rotation of the molecules in a direction perpendicularly to their longitudinal axis. In the case of liquid-crystalline materials in the so-called cholesteric phase, the pitch of the rotation is 0.1 to 1 μm . For application in, for example, datagraphic displays using multiplex drive, a larger pitch of the order of magnitude of
35 the cell thickness or even more of the display device is desirable. Such a

pitch, also called cholesteric pitch referring to chiral nematic or cholesteric LCs, is obtained by adding a chiral compound which also can be a liquid-crystalline compound itself as a dopant to a nematic liquid crystal. With such materials, supertwisted nematic (STN) liquid-crystal display devices are manufactured, the total twist of the molecular axis across the cell being, for example, between 180° and 270° . Such display devices have the disadvantage that the optical properties depend to a large extent on the wavelength, of the light so that a high contrast and a colourless image (black/white instead of e.g., blue/yellow) is difficult to attain. Said disadvantage can be overcome in a known manner by using a combination of two identical cells, one of which contains left-handed liquid-crystalline material and the other contains right-handed liquid-crystalline material. When the molecular axis at the front of the second cell extends perpendicularly to the molecular axis at the rear of the first cell the wavelength dependence of the optical properties is completely compensated. However, as a result of this second cell the liquid-crystal display device becomes heavier and less compact. According to a simpler alternative, the second cell is replaced by a uniaxial foil having an adapted birefringence. In this case, the compensation of the wavelength dependence is not complete, resulting in the display device exhibiting a contrast reduction and a certain degree of colour e.g. in the voltageless state. Another alternative consists in the use of a twisted stack of uniaxial foils. This solution gets closer to the ideal situation (a twist and a birefringence which are equal to the twist and birefringence of a supertwisted nematic liquid-crystal display device) as the number of foils increases. However, this leads to a considerably more complicated production process. Instead of a foil, it is alternatively possible to use a birefringent layer on a suitable substrate. In European Patent Application 91-0 007 574 a description is given of liquid-crystalline polymer materials having a chiral dopant in the form of a copolymerizable monomer. Such polymer materials are linear and have side groups which exhibit liquid-crystalline properties. A thin layer is manufactured from a solution or a melt and is oriented in the rubbery liquid-crystalline state, after which it is cooled to a temperature below the glass transition temperature. Such layers are often turbid owing to local fluctuations in the refractive index

caused by a poor orientational order. Moreover, heating the material above the glass transition temperature, even when executed only once, leads to a permanent loss of order. Besides, the method does not permit the pitch and the thickness of the polymer layer to be accurately adjusted.

5

In the U.S. patent No. 5,210,630 a polymeric film for display devices is disclosed obtained from polymerization of a mixture of monomers having at least two polymerizable groups in the presence of a chiral dopant. However, it is not possible to compensate the temperature dependence of the optical pathway of the low-molecular weight liquid crystals in the display with the aid of that film.

10

One of the objects of the invention is to provide a polymeric film for liquid-crystal display devices being optically clear and having a large temperature resistance. Another object of the invention is to provide a supertwisted nematic liquid-crystal display device having a high contrast, the voltageless state being substantially completely dark and colourless, and the voltage on state being highly transparent. Another object of the invention is to provide a compensation film for a TN, a IPS, a ASM or a similar LC device.

15

20

A further object of the invention is to provide a film which can be manufactured with the desired accuracy in a simple manner.

25

Another object of the invention is to provide a material which can be suitably be used in the film.

30

The general object of the invention is to provide a film whose optical properties are not too dissimilar to those of the LC within the LC cell.

According to the invention, these objects are achieved by a polymeric film as described in the opening paragraph, characterized in that it is obtainable by copolymerization of a mixture comprising

35

- 5 (a) at least one monomer or oligomer, each of said monomers or oligomers having at least two polymerizable functional groups selected from the group consisting of (meth-)acrylate ester, epoxy and vinyl ether,
- (b) at least one achiral liquid crystalline monomer or oligomer, each of said monomers/oligomers having mesogenic groups and one polymerizable functional group selected from the group consisting of (meth-)acrylate ester, epoxy and vinyl ether,
- 10 (c) a photoinitiator,
- (d) additives selected from inhibitors and accelerators,
- 15 (e) optionally at least one chiral component which is preferably a liquid crystalline compound or is compatible with liquid crystalline phases, and
- (f) optionally at least one liquid-crystalline mono- or dithiol compound.
- 20

The synthetic resin composition is preferably manufactured from a curable liquid-crystalline composition having a chiral dopant.

25 In a preferred embodiment of the polymeric film according to the invention, the synthetic resin composition is formed by curing a mixture of liquid-crystalline monomers or oligomers which consist of compounds (a) with two or more acrylate-ester groups and compounds (b) with one acrylate ester group. Instead of acrylate compounds, epoxides, vinyl ethers and thiolene compounds can alternatively and satisfactorily be used as liquid-

30 crystalline monomers.

Further preferred embodiments are:

- 5 a) A polymeric film wherein each of said monomers or oligomers of group (a) have at least two (meth-)acrylate-ester groups and each of said monomers or oligomers of group (b) have one (meth-)acrylate-ester group.
- 10 b) A polymeric film wherein the optically anisotropic material comprises at least one mesogenic chiral additive (e).
- 15 c) A polymeric film preferably containing a thiol which is preferably a monothiol especially a liquid crystalline or liquid crystal-like thiol, whose purpose is to limit the molecular weight of the resultant polymer. These thiol compounds terminate the free radical initiated polymerization.
- 20 d) A polymeric film being obtainable by in-situ UV co-polymerization of a mixture comprising at least one monomer or oligomer of group (a), at least one monomer or oligomer of group (b), at least one UV initiator (c) and at least one chiral additive (e).
- 25 e) A polymeric film wherein the optically anisotropic material comprises
- 5-50 % by weight of at least one monomer or oligomer of group (a)
 - 20-95 % by weight of at least one monomer or oligomer of group (b),
 - 30 - 0,5-5 % by weight of a photoinitiator (c),
 - 1-20 % by weight of at least one chiral additive (e), and
 - 35 - 1-20 % by weight of at least one liquid crystalline monothiol compound (f).

- f) A polymeric film wherein each of said monomers or oligomers of group (a) have a mesogenic group.

5

It has been found in our extensive investigations that the degree of possible movement in a side group LC polymer is in the first approach dependent on the molecular weight of the polymers. 'Small' polymers have faster response times than polymers with a high molecular weight [MWt].

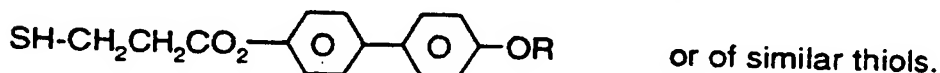
10

In order to mimic a low molar mass LC with respect to its thermal fluctuations it is desirable for the side groups on an LC polymer to be as freely movable as possible. This is accomplished by using a low MWt polymer which is achieved by using thiols to terminate polymerization. Typically one would have to use 10-15 % of such a thiol to produce the desired lower MWt materials.

15

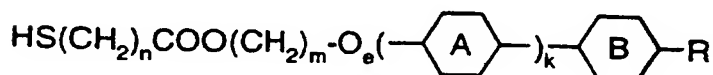
In practice conventional thiols are not very soluble in the polymer precursors and phase separate at 5 % or even at lower concentrations (i.e. octylthiol $C_8H_{17}SH$). However, this problem is overcome by using a liquid crystalline thiol as e.g.

20



25

Typical thiols used according to the present invention are of the following structure:

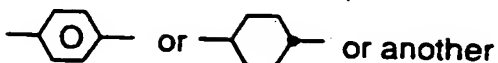
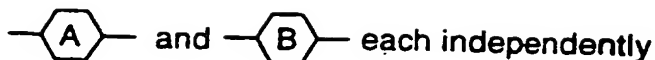


30

with

$$\begin{aligned} n &= 1 \text{ to } 6 \\ m &= 0 \text{ to } 10 \\ e &= 0 \text{ or } 1 \\ k &= 0 \text{ or } 1 \end{aligned}$$

35



5

6-membered 1-4 disubstituted ring which can also bear one or more lateral groups like R or F

R = C₁ to C₉ alkyl, alkenyl, oxyalkyl or oxyalkenyl.

10

Adding a chiral substance twists the molecular axis of the LC chain. A layer of the material thus obtained exhibits a nematic order, with a helical structure, also termed cholesteric order. The natural pitch of the mixture depends on the type and the quantity of the chiral dopant added and is approximately 28 μm at 0.5 mol % and approximately 2.5 μm at 6 mol % for typical dopants like S-811 of Merck KGaA, Germany.

15

20

The curable synthetic composition is cured by photopolymerization using exposure to actinic radiation e.g. ultraviolet light for typically 3 minutes produced by a short-arc mercury lamp at 50 °C having a radiation intensity on the surface to be cured from 2 to 5 mW/cm². During curing the orientation is fixed, the overall rotation angle of the layer remaining constant. The rotation angle is a measure of the number of revolutions in the molecular spiral in the cholesteric nematic phase. For this reason, the variation in pitch during curing depends only on the change in layer thickness as a result of possible polymerization shrinkage.

25

30

In the polymerization operation substantially no change takes place in the product $d\Delta n$ d being the layer thickness and Δn being the birefringence of the material. As the material shrinks in only one direction during polymerization, the change in layer thickness is inversely proportional to the change in density of the material, which latter quantity is proportional to the degree of birefringence.

35

The rotation angle of the polymer film thus obtained exhibits no temperature dependence in the range from room temperature to

250 °C demonstrating the complete resistance to molecular re-orientation as a result of the network of polymer molecules formed by cross-linking. As the monomers partly contain two acrylate-ester groups per molecule, cross-linking is so strong that only little movement is possible in the rigid parts of the liquid-crystalline molecules.

In comparison with, for example, cholesteric polymers having chiral groups in side chains, the pitch has a small temperature dependence.

Within certain limits, the pitch can be influenced by curing the synthetic resin composition between two substrates. Having a cladding of an orienting material such a rubbed polyimide the polyimide surface is rubbed uniaxially, for example with a velvet cloth. The pitch depends on the distance between the two substrates, according to this example, 6 μm , and the angle between the two directions of rubbing the polyimide surfaces. The number of revolutions of the molecular spiral adjusts itself such that the pitch obtained does not differ much from the natural pitch.

However, very low MWt LC polymers melt to fluid polymers but by cross linking the short low MWt LCP's by a small amount of a difunctional material the overall MWt can be increased but one still retains a fast or easy movement of the side groups.

We further have observed that the molecular weight of the LC polymer forming the film is not the only and may be even not the most important parameter of the polymer influencing its wavelength dispersion of the optical anisotropy. As this dispersion and its temperature dependence should be as close to that of the low molecular mass LC used in the active (i.e. the driven) LC cell of the display which may be e.g. a TN, a STN or another mode as e.g. in plane switching (IPS), or other LCDs, the LC polymer should be of similar nature and orientational order to these low molecular LCs.

5 The probably most decisive parameter of the polymer LCs in this
respect seems to be the "average linear chain length" which can be
derived e.g. from the amount of the thiol used in the formulation of the
precursors, considering especially its functionality and its
concentration. The relevance of this "average linear chain length" may
be visualized as follows: The low molecular weight LCs are rather
freely movable, e.g. can rotate and translate more easily, compared to
typical LC polymers, leading to a different dispersion and a different
10 temperature dependence of the dispersion. This is due to the fixation
of the LC units in the LC polymer, which may be more or less rigid
from case to case but is always more rigid than that in a monomeric
LC. Considering a side group LC polymer, the LC side groups in the
middle of the chain are much more restrained in their movements by
the polymer backbone and the other side groups at each side and
15 from similar groups in other polymer chains than those LC side groups
close to the end of the chain. These side groups at the end of a chain
do not have such severe restrictions and consequently behave more
like low molecular mass LC molecules. Thus the closer a side group is
located to the end of a chain, the more it behaves as desired here, i.e.
20 like low molecular mass LC.

As the birefringent side groups of the new compensator layer should
behave similar to the LC cell e.g. an STN cell or maybe also an axially
25 symmetric mode (ASM) cell, short polymer chains of e.g. 5 to 50 units
and preferably of 10 to 30 and most preferred of 10 to 20 units length
are required. These then in fact lead to a higher concentration of end
groups.

30 Polymer chains in the state of the art which are produced by in-situ
photopolymerization have typical lengths of about 200 to 300 units.
However, LC polymers with the short chain lengths desired for our
type of application very often suffer from softening which is
unfavorable for practically usable films. This suffering is diminished or
35 even avoided by cross-linking the short chains of the polymer

together. This does increase the MWt of the polymer but it does not change the effective length of the chains and consequently does not change the end group density, at least not significantly.

5 Thus monoreactive thiols are beneficially used to achieve the desired chain lengths and/or at least direactive thiols to crosslink the short chain polymers. Cross-linking however is preferably achieved e.g. by direactive acrylates, epoxydes or enes.

10 Hence, such a polymer is an excellent compensation foil for e.g. STN and TN, in plane switching, axially symmetric mode and other AM LCDs.

15 Most preferred are STN and AM LCDs. The preferred mode of the AM LCDs is the TN mode. In another embodiment the LC mode is the "in plane switching" or IPS mode as described e.g. in EP 0 509 026 and EP 0 588 568. Also the "axially symmetric aligned microdomain" or ASM mode as described in EP 0 568 355, EP 0 626 607 and JP 6-301 015 A (Kokai, laid open No.) is preferred.

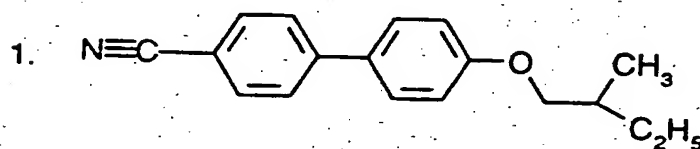
20 Both these and other modes can be used in directly driven displays too, just as TN and STN mode.

25 An ordered synthetic resin composition can be obtained, for example, by orienting a liquid-crystalline monomer mixture and freezing said orientation by exposure to UV light in the presence of a light-sensitive initiator, as in principle disclosed by EP 0 445 629.

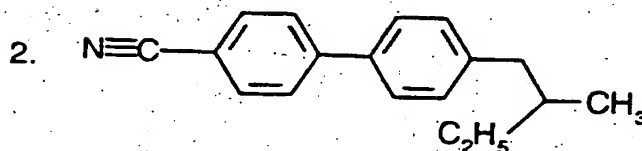
30 A chiral component (e), for example, a compound with an asymmetrically substituted carbon atom can be added to the monomer. This dopant brings about a rotation of the monomer molecules in a direction perpendicular to the longitudinal axis of the molecules. By arranging the monomer between two polyimide-coated and rubbed surfaces or other orienting surfaces such as obliquely
35 deposited SiO₂, the degree of orientation or rotation can be adjusted

as a function of the natural pitch (the pitch without the presence of such surfaces), the distance between the rubbed surfaces and the direction of rubbing of the surfaces. Subsequently, the crystalline rotation in the still liquid monomer composition is fixed by polymerization of the reactive end groups under the influence of UV light or irradiation using electrons. The desired order is rapidly obtained and is substantially perfect, so that a clear film or thin layer is attained. As a result of the use of a mixture of monomers having at least two functional groups (a) and of monomers having only one functional group (b) an ordered polymer network is maintained up to very high temperatures.

Compounds suitable as chiral dopants for the polymer precursor are, for example:



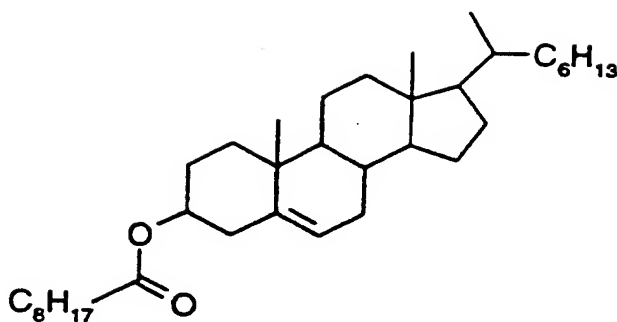
C 15



CB 15

5

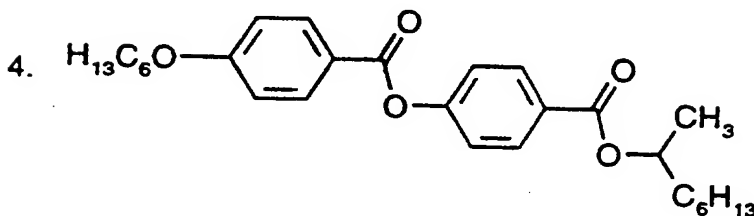
3.



10

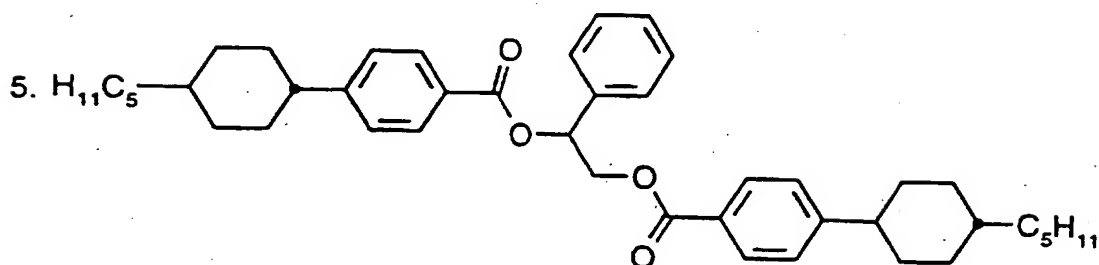
CN

15



S-811 / R-811

20



25

S-1011 / R-1011

30

Other chiral dopants are known to the experts. In a preferred embodiment of the present invention an enantiomeric pair of chiral molecules is used as dopants, one enantiomer for low molecular weight LC in the LC cell and its mirror molecule, the enantiomer with the opposite configuration, for the polymer precursor. Such pairs are known to the expert. A typical example is S-811 and R-811 of Merck

35

KGaA, Germany, where S-811 has negative helical twisting power inducing left-handed twist. Also combinations of chiral dopants are used with beneficial effects, e.g. reducing the temperature dependence of the pitch.

Since the mixtures of monomers or oligomers for obtaining the polymeric film according to the present invention exhibit, as a rule, broad nematic or cholesteric mesophases with melting points at comparable low temperatures, the inventive film may be produced by irradiation at comparable low temperatures (below 100 °C preferably between 30 and 80 °C). If desirable, the curable synthetic resin composition may comprise a mixture of various oligomeric compounds. Besides, the synthetic resin composition may comprise one or more other suitable components such as, for example, catalysts, (light-sensitive) initiators, stabilizers, co-reacting monomers and surface-active compounds. It is alternatively possible to add, for example, a quantity of up to 50 % by weight of a nonpolymerizable liquid-crystalline material to adapt the optical properties of the material.

Suitable compounds (a) are known from U.S. Pat. No. 4,758,447. In the application described although, no helicoidal order is pursued. A method of manufacturing suitable compounds is described in European Patent 0 261 712. Suitable compounds (a) and (b) are disclosed for example in WO 93/22 397; further suitable compounds (b) are disclosed for example in EP 0 590 376.

As a rapid curing of the composition is desired, the curing operation is initiated, preferably, by means of actinic radiation. The expression actinic radiation is to be understood to mean herein radiation using light, in particular UV light, X-rays, gamma rays or radiation using high-energy particles such as electrons or ions. The geometry of the display device, in particular a TN, STN, IPS or ASM device, is conventional.

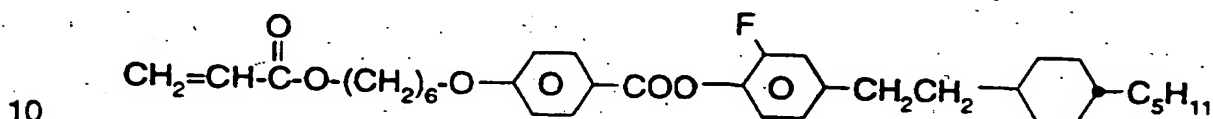
Films according to the present invention are easily modified with respect to adaption of the optical retardation $d \cdot \Delta n$ to that of the LC cell to be compensated, e.g. by modification of the layer thickness or the composition of the polymer precursor, which are both variable over a wide range. The adaption can be achieved either to the on states or to the off states of the active cells or to an intermediate partially switched state, as desired. the desired twist angle of the molecules of the compensation film can be achieved by modification of the chiral dopant used and its concentration. Especially preferred are single chiral compounds, which are cholesteric liquid crystals or are compatible with the liquid crystalline precursor of the polymer film of the compensator. Especially preferred are single chiral compounds or combinations of chiral compounds of preferably two and less preferably more than two chiral compounds which have a small temperature dependence of the cholesteric pitch in the polymer precursor, as they do not lead to a very stringent requirement for the temperature control during the curing of the polymer precursors. They further allow to vary the curing and processing temperatures easily and over wide temperature ranges without influencing the resultant pitch and consequently the twist of the compensator.

The films do not have to be contained between two substrates for curing. In a preferred embodiment free standing thin films supported by one substrate with an orientation layer are cured.

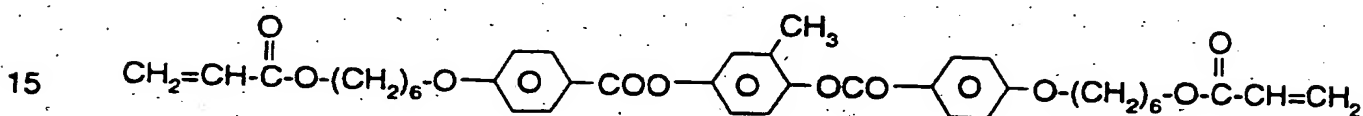
Examples

Example 1

5 A starting mixture for a curable composition is manufactured from 84 parts by weight of a mono acrylate compound A



15 parts by weight of a diacrylate compound B



20 and 1 part by weight of a light-sensitive initiator, in the present example 2,2-dimethoxy-2-phenyl-acetophenone, commercially available from Ciba-Geigy under the trade name Irgacure® 651 (IRG 651). A method of manufacturing the diacrylate compounds is described in EP-0 261 712 and for the monoacrylate in EP 0 590 376. The starting mixture additionally comprises 100 ppm of a stabilizer, for example hydroquinone monomethyl ether.

25 The starting mixture is a composition having a melting point of 38.2 °C, above which exists a nematic phase which changes into an isotropic phase at a temperature of 123.3 °C. The mixture is used, coated and cured at a temperature between these two temperatures, the highest viscosity and highest molecular order being obtained at the lowest temperatures.

30 The mixture is cured at 80 °C with 6 mW/cm² at 365 nm (+/- 7 nm FWHM) after spincoating and evaporation of the solvent. The resulting film has no chiral twist or in other words an infinite cholesteric pitch as no chiral additive had been used.

Example 2

According to the present example, different quantities of a chiral dopant can be added to the starting mixture, for example left-handed 4-(4-hexyloxy-benzoyloxy)-benzoic acid-2-octylester commercially available from Merck under the number S-811. The chiral dopant itself may not have to exhibit liquid-crystalline properties, and may be both a copolymerizing monomer and a nonpolymerizable compound. To obtain a twisted nematic order in the polymer it is sufficient for the compound to be chiral. The chiral dopant may be left-handed or right-handed.

For Example 2 14 % of the diacrylate B were used together with 84.2 % of the monoacrylate A, 1 % of the photoinitiator IRG 651 and 0.8 % of the chiral dopant S-811, all concentrations are given in mass%. It was cured after solvent (toluene) evaporation, under dry nitrogen at a temperature of 75 °C for 10 minutes with 5 mW at 370 nm (+/- 10 nm). The results are listed in the following Table 2.

The films prepared were applied to typical STN cells all with the appropriate twist angle of either 180°, 240° or 270° and 5° surface pretilt angle (2° to 3° pretilt for 180° twist) filled with the liquid crystal mixture ZLI-2293, a sales product of Merck KGaA of Germany, doped with the chiral dopant R-811, i.e. the enantiomer of S-811 to a d/p value of 0.5 or 0.55 for the 270° twisted cells. The match respectively mismatch of the dispersions were observed both by determining the dispersion of the film and the LC cell individually as well as by that of the combined display element. The Example 1 as well as Examples 2 and 3 can be looked upon as comparative examples. The precursor components used are summarized in Table 1, whereas the results are listed in Table 2.

Examples 3 to 8

These examples contain some thiol to limit the MWt and the average linear chain lengths of the LC polymer of the compensation film.

The films were made like for Example 1 by solvent coating i.e. spin coating solutions of the components in toluene onto a rubbed polyimide surface, subsequent evaporation of the solvent at an elevated temperature followed by UV exposure under a nitrogen atmosphere at 70 to 80 °C, of $\lambda = 360$ to 380 nm, 5 to 20 mW/cm².

Table 1 : Polymer Precursors

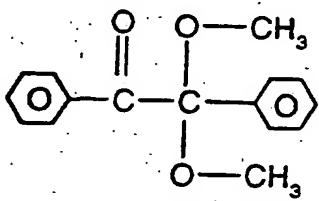
Compound	n	Structure
Diacrylate A	3	$\text{CH}_2=\text{CHCO}_2(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{OOC}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_n\text{O}_2\text{CCH}=\text{CH}_2$
Diacrylate B	6	$\text{CH}_2=\text{CHCO}_2(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{OOC}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_n\text{O}_2\text{CCH}=\text{CH}_2$
Monoacrylate B	6	$\text{CH}_2=\text{CHCO}_2(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_3\text{H}_7$
Thiol A	6	$\text{HSCH}_2\text{CH}_2\text{CO}_2(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_3\text{H}_7$
Photoinitiator IRG 651	-	

Table 2: Results for Examples

Examples	EX 2	EX 3	EX 4	EX 5	EX 6	EX 7	EX 8
(a ₁) diacrylate A (%)	-	13.9	5	5	3	5	-
(a ₂) diacrylate B (%)	14	-	-	-	2	-	5
(b ₁) monoacrylate A (%)	84.1	-	-	-	-	-	-
(b ₂) monoacrylate B (%)	-	84	87.9	82.9	82.9	87.9	82.9
(c) thiol A (%)	-	-	5	10	10	5	10
(d) IRG 651 (%)	1	1	1	1	1	1	1
(e) S-811 (%)	0.8	1.1	1.1	1.1	1.1	1.25	1.1
Av linear chain length	~200	~200	20	10	10	20	15
Film thickness	6 μ m	6 μ m	6 μ m	6 μ m	6 μ m	6 μ m	6 μ m
Helical twist	180°	240°	240°	240°	240°	270°	240°
Dispersion Match LC	poor	poor	good	good	good	good	good
Temp. dep.	poor	very poor	moderate	good	good	good	moderate

These examples can easily be varied by the expert. For example by using a smaller concentration of the chiral dopant the twist of the compensating layer can be adjusted to 90° matching a typical TN device. The adaption of the optical and chiral properties of the compensator to various types of LCDs including amongst others IPS and ASM devices is obvious to the expert from their respective molecular arrangements in the cells either in the off, the on or any partially switched state.

Claims

1. A polymeric film composed of an optically anisotropic material made from a cross-linked synthetic resin composition comprising a polymer network, being obtainable by copolymerization of a mixture comprising
- 5
- (a) at least one monomer or oligomer, each of said monomers or oligomers having at least two polymerizable functional groups selected from the group consisting of (meth-)acrylate ester, epoxy and vinyl ether,
- 10
- (b) at least one achiral liquid crystalline monomer or oligomer, each of said monomers/oligomers having mesogenic groups and one polymerizable functional group selected from the group consisting of (meth-)acrylate ester, epoxy and vinyl ether,
- 15
- (c) a photoinitiator,
- 20
- (d) additives selected from inhibitors and accelerators,
- (e) optionally at least one chiral component, and
- (f) optionally at least one liquid-crystalline mono- or dithiol compound.
- 25
2. The polymeric film of claim 1 wherein each of said monomers or oligomers of group (a) have at least two (meth-)acrylate-ester groups and each of said monomers or oligomers of group (b) have one (meth-)acrylate-ester group.
- 30
3. A polymeric film of claim 1 or 2 wherein the optically anisotropic material comprises at least one mesogenic chiral additive (e).
- 35

4. A polymeric film of any of the preceding claims being obtainable by in-situ UV co-polymerization of a mixture comprising at least one monomer or oligomer of group (a), at least one monomer or oligomer of group (b), at least one UV initiator (c) and at least one chiral additive (e).
- 5
5. A polymeric film of any of the preceding claims wherein the optically anisotropic material comprises
- 10
- 5-50 % by weight of at least one monomer or oligomer of group (a)
 - 20-95 % by weight of at least one monomer or oligomer of group (b),
 - 15
 - 0,5-5 % by weight of a photoinitiator (c),
 - 1-20 % by weight of at least one chiral additive (e), and
 - 20
 - 1-20 % by weight of at least one liquid crystalline monothiol compound (f).
6. A polymeric film of any of the preceding claims wherein each of said monomers or oligomers of group (a) have a mesogenic group.
- 25
7. A liquid crystalline device comprising a liquid-crystal cell having a twisted nematic liquid-crystal material arranged between two electrodes and a film for compensation of the birefringence of the liquid-crystal material characterized in that said compensation film is a
- 30
- polymeric film of any of the claims 1 to 5.
- 35

INTERNATIONAL SEARCH REPORT

International Application No
CT/EP 96/00646

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K19/54 C08F220/00 C09K19/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, P	EP, A, 0 643 121 (PHILIPS ELECTRONICS) 15 March 1995 see column 1, line 45 - column 3, line 15 see column 3, line 31 - line 56 see column 4, line 23 - line 36; figure 2 ---	1-4, 6, 7
Y	EP, A, 0 451 905 (PHILIPS) 16 October 1991 see column 2, line 13 - column 3, line 6 see column 5, line 22 - line 50 ---	1-4, 6, 7
A, P	EP, A, 0 648 827 (MERCK) 19 April 1995 see page 3, line 50 - page 4, line 21; examples 1-5 --- -/-	1, 6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

7 June 1996

Date of mailing of the international search report

24.06.1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Boulon, A.

INTERNATIONAL SEARCH REPORT

Final Application No

PCT/EP 96/00646

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>MOLECULAR CRYSTALS AND LIQUID CRYSTALS (INC. NONLINEAR OPTICS), vol. 200, 1 May 1991, pages 197-204, XP000258411 HIKMET R A M ET AL: "CHOLESTERIC NETWORKS CONTAINING FREE MOLECULES" ---</p>	1,3,4
A	<p>DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-348515 XP002005086 & JP,A,05 255 460 (NIPPON KAYAKU) see abstract -----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/00646

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-643121	15-03-95	BE-A- 1007485 JP-A- 7168148	11-07-95 04-07-95
EP-A-451905	16-10-91	NL-A- 9000808 JP-A- 4227684 US-A- 5188760	01-11-91 17-08-92 23-02-93
EP-A-648827	19-04-95	NONE	

THIS PAGE BLANK (USPTO)